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February 12, 2002

**BOX PCT**Commissioner for Patents  
Washington, D.C. 20231

PCT/JP99/05363

-filed September 30, 1999

Re: Application of Akihiro GOTO and Toshio MORO  
DISCHARGE SURFACE TREATMENT ELECTRODE, MANUFACTURING  
METHOD THEREOF AND DISCHARGE SURFACE TREATING METHOD  
**Assignee: MITSUBISHI DENKI KABUSHIKI KAISHA**  
Our Ref: Q67947

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- ☒ an executed Declaration and Power of Attorney.
- ☒ an English translation of the International Application.
- ☒ seven (7) sheets of drawings.
- ☒ an English translation of Article 34 amendments (annexes to the IPER).
- ☒ an executed Assignment and PTO 1595 form.
- ☒ Information Disclosure Statement and PTO Form 1449 and references.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	<u>7</u>	-	<u>20</u>	=		x	\$18.00	=	<u>\$0.00</u>
Independent claims	<u>3</u>	-	<u>3</u>	=		x	\$84.00	=	<u>\$0.00</u>
Base Fee									<u>\$890.00</u>

<b>TOTAL FILING FEE</b>	<u>\$890.00</u>
<b>Recordation of Assignment</b>	<u>\$ 40.00</u>
<b>TOTAL FEE</b>	<u>\$930.00</u>

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Checks for the statutory filing fee of \$890.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Respectfully submitted,

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Description

DISCHARGE SURFACE TREATMENT ELECTRODE, MANUFACTURING METHOD  
THEREOF AND DISCHARGE SURFACE TREATING METHOD

Technical Field

This invention relates to improvements in a discharge surface treatment electrode and a manufacturing method thereof and a discharge surface treatment method used for discharge surface treatment for causing discharge to occur between the electrode and a workpiece and forming a hard film made of electrode material on the workpiece surface by the discharge energy or a hard film made of a substance resulting from the electrode material reacting with by the discharge energy on the workpiece surface.

Background of the Invention

Hitherto, a discharge surface treatment method, for example, disclosed in JP-A-5-148615 has been available as an art of forming a hard film on a workpiece surface for providing corrosion resistance and abrasion resistance. This art provides a discharge surface treatment method of metal material consisting of two steps of performing primary working (laying-up working) using a compacted powder electrode of a discharge surface treatment electrode comprising WC (tungsten carbide)

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powder and Co (cobalt) powder mixed and compressed and molded and then replacing the electrode with an electrode comparatively less quickly consumed such as a copper electrode and performing secondary working (re-melt working). This method can form a hard film having strong adhesion to a copper material, but is difficult to form a hard film having strong adhesion to a sintered material such as a hard alloy.

However, our study finds out that if a material for forming hard carbide such as Ti (titanium) is used as a discharge surface treatment electrode and discharge is caused to occur between the electrode and a metal material of a workpiece, a hard film can be formed on the metal surface of the workpiece without a re-melt step. The reason why a strong hard film can be formed is that with the discharging, the consumed electrode material and C (carbon) of a component of work liquid react with each other to produce TiC (titanium carbide). It is also found out that if discharge is caused to occur between a compacted powder electrode of a discharge surface treatment electrode made of metal hydride such as TiH<sub>2</sub> (titanium hydride) and a metal material of a workpiece, a hard film can be formed more rapidly and with higher adhesion as compared with the case where Ti etc. is used as the material. Further, it is found out that if discharge is caused to occur between a compact powder electrode of a discharge surface treatment electrode comprising any other metal or ceramics mixed with hydride such as TiH<sub>2</sub>

and a metal material of a workpiece, a hard film having various properties of hardness, abrasion resistance, etc., can be formed more quickly.

Such a method is disclosed, for example, in JP-A-192937/1997. A configuration example of a discharge surface treatment electrode and an apparatus used for such discharge surface treatment will be discussed with reference to FIG. 7. In the figure, numeral 1 denotes a compacted powder electrode of a discharge surface treatment electrode comprising  $TiH_2$  powder compressed and molded, numeral 2 denotes a workpiece, numeral 3 denotes a work tank, numeral 4 denotes work liquid, numeral 5 denotes a switching element for switching voltage and current applied to the compact powder electrode 1 and the workpiece 2, numeral 6 denotes a control circuit for controlling turning on/off the switching element 5, numeral 7 denotes a power supply, numeral 8 denotes a resistor, and numeral 9 denotes a formed hard film. According to such a configuration, discharge is caused to occur between the compact powder electrode 1 and the workpiece 2 and the hard film 9 can be formed by the discharge energy on the surface of the workpiece 2 made of steel, a hard alloy, etc.

Such formation of a hard film made of carbide, etc., on a workpiece by discharge surface treatment is executed by forming a film of carbide on the workpiece by heat energy of discharge using the carbide which becomes the component of the hard film

to be formed as a component of the discharge surface treatment electrode or by using metal containing the carbide which becomes a component of the hard film to be formed or a compound of that metal as the component of the discharge surface treatment electrode and causing the metal or the metal compound to react with a component of work liquid, C, by heat energy of discharge to form a hard film made of carbide on the workpiece.

Here, if the component of the discharge surface treatment electrode is only a material having comparatively high hardness such as carbide, powder of the discharge surface treatment electrode component cannot be fixed by compression molding of press and thus usually a material having comparatively low hardness is mixed as a binder. However, if Co (cobalt), etc., used as a binder to manufacture a sintered alloy, etc., is mixed as an electrode material, it is a material not producing carbide and thus the hardness of a hard film formed on a workpiece becomes low and the material cannot be used for such application where high abrasion resistance is required; this is a problem. Some materials in the hard film formed on the workpiece may be poor in compatibility with the base material of the workpiece and in such a case, there is a problem of weakening the adhesive strength of the hard film.

#### Disclosure of the Invention

It is an object of the invention to solve the

above-mentioned problems and provide a discharge surface treatment electrode and a manufacturing method thereof and a discharge surface treatment method capable of enhancing the hardness and strength of a hard film formed on a workpiece by discharge surface treatment.

According to the invention, there is provided a discharge surface treatment electrode used for discharge surface treatment causing discharge to occur between the electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on the surface of the workpiece by discharge energy, wherein the metal carbide and metal contained in the metal carbide or a compound of that metal or any other metal forming the hard carbide or a compound of that metal are contained as material of the discharge surface treatment electrode.

The metal carbide is metal carbide of metal or a metal compound contained in material of the workpiece.

The material of the discharge surface treatment electrode contains WC and W.

According to the invention, there is provided a manufacturing method of a discharge surface treatment electrode used for discharge surface treatment causing discharge to occur between the electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on a surface of the workpiece by discharge energy,

wherein powder of the metal carbide and powder of metal contained in the metal carbide or powder of a compound of the metal or powder of any other metal forming hard carbide or powder of a compound of the metal are mixed and are compressed and molded to form the discharge surface treatment electrode.

Wax is added to the material of the discharge surface treatment electrode and then they are compressed and molded and are heated at a temperature at least as high as that at which the wax is melted and no higher than the temperature at which the wax is decomposed to produce soot, for evaporating and removing the wax to form the discharge surface treatment electrode.

According to the invention, there is provided a discharge surface treatment method for causing discharge to occur between a discharge surface treatment electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on the surface of the workpiece by discharge energy, wherein a discharge surface treatment electrode containing the metal carbide and metal contained in the metal carbide or a compound of that metal or any other metal forming hard carbide or a compound of that metal is used.

The metal carbide is metal carbide of metal or a metal compound contained in material of the workpiece.

The invention is configured as described above and thus has the advantage that the hardness and strength of a hard film



formed on a workpiece by the discharge surface treatment can be enhanced.

#### Brief Description of the Drawings

FIG. 1 is a sectional view to show the concept of a discharge surface treatment electrode and a manufacturing method thereof according to embodiment 1 of the invention.

FIG. 2 is a drawing to show a discharge surface treatment method according to embodiment 1 of the invention.

FIGS. 3A and 3B are schematic representations to show how a hard film is formed on a workpiece by the discharge surface treatment method according to embodiment 1 of the invention.

FIG. 4 is a schematic representation to show another example of the discharge surface treatment method according to embodiment 1 of the invention.

FIGS. 5A and 5B are schematic representations to show the concept of a manufacturing method of a discharge surface treatment electrode according to embodiment 2 of the invention.

FIG. 6 is a drawing to show an example of a vapor pressure curve of wax mixed with discharge surface treatment electrode material at the compressing and molding time of the discharge surface treatment electrode according to embodiment 2 of the invention.

FIG. 7 is a drawing to show a configuration example of a discharge surface treatment electrode and an apparatus in

a related art.

## Best Mode for Carrying out the Invention

### Embodiment 1

FIG. 1 is a sectional view to show the concept of a discharge surface treatment electrode and a manufacturing method thereof according embodiment 1 of the invention. In the figure, numeral 10 denotes a discharge surface treatment electrode, numeral 11 denotes WC (tungsten carbide) powder, numeral 12 denotes W (tungsten) powder, numeral 13 denotes an upper punch of a mold, numeral 14 denotes a lower punch of the mold, and numeral 15 denotes a mold die. The WC powder 11 and the W powder 12 are mixed and entered in the press mold and compressed and molded, thereby forming the discharge surface treatment electrode 10.

To enhance the hardness of a hard film formed on a workpiece, it is desirable that the component of the discharge surface treatment electrode should be only a material having comparatively high hardness such as carbide to make the film component of only a material having higher hardness, as previously described in Background of the Invention. Some material of the hard film formed on the workpiece may be poor in compatibility with the base material of the workpiece and a problem of weakening the adhesive strength of the hard film, etc., may occur. Thus, a material having good compatibility with the base material of the workpiece needs to be mixed in

the discharge surface treatment electrode.

In the invention according to embodiment 1, to make the film component of only a material having higher hardness and provide good compatibility between the base material of the workpiece and the hard film formed on the workpiece, as discharge surface treatment electrode material, powder of hard metal carbide having higher hardness and powder of material contained in the base material of the workpiece and reacting with C (carbon) contained in work liquid to form the above-mentioned hard carbide are mixed and compressed and molded for forming a discharge surface treatment electrode.

For example, the discharge surface treatment electrode 10 in FIG. 1 shows the case where a sintered hard alloy of a sintered material of WC and Co are the main materials of the workpiece. The hardness of the sintered hard alloy is HV= about 1300 to 2000 as micro Vickers hardness, because the whole hardness is degraded since soft Co is mixed although the hardness of WC is HV=about 2400. The discharge surface treatment electrode 10 in FIG. 1 consists of WC and W, and a film of only WC having higher hardness can be formed on the workpiece by discharge surface treatment using the electrode. WC is the same material as the component of the sintered hard alloy and thus has good compatibility with the sintered hard alloy of the base material and can provide strong adhesion. FIG. 2 shows a discharge surface treatment method according to embodiment 1 of the

invention, and FIGs. 3A and 3B show how a hard film is formed on a workpiece by the discharge surface treatment method according to embodiment 1 of the invention. In the figures, numeral 3 denotes a work tank, numeral 4 denotes work liquid containing C as a component thereof, numeral 10 denotes a discharge surface treatment electrode consisting of WC and W, numeral 16 denotes a workpiece of a sintered hard alloy, numeral 17 denotes a discharge surface treatment power unit, numeral 18 denotes an arc electrode of discharge, numeral 19 denotes a discharge surface treatment electrode component melted by discharge heat and moved to the workpiece side, and numeral 20 denotes a hard film made of WC. When discharge occurs between the discharge surface treatment electrode 10 and the workpiece 16 by the discharge surface treatment power unit 17 in FIG. 2, the discharge surface treatment electrode 10 is melted by discharge heat and is emitted between electrodes and the discharge surface treatment electrode component 19 melted by discharge heat and moved to the workpiece side is deposited on the workpiece 16, as shown in FIG. 3A. Next, W of the component of the discharge surface treatment electrode 10 reacts with C of the component of the work liquid 4 to produce WC and together with WC of the component of the discharge surface treatment electrode 10 the hard film 20 made of WC is formed on the workpiece 16, as shown in FIG. 3B.

FIG. 4 shows another example of the discharge surface

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treatment method according to embodiment 1 of the invention; it shows the case where the workpiece is a steel material. In the figure, numeral 3 denotes a work tank, numeral 4 denotes work liquid containing C as a component thereof, numeral 17 denotes a discharge surface treatment power unit, numeral 18 denotes an arc electrode of discharge, numeral 21 denotes a discharge surface treatment electrode consisting of WC and Fe (iron), and numeral 22 denotes a workpiece of a steel material. Thus, to form a film on the workpiece 22 of a steel material, Fe of the base material of the workpiece 22 is mixed as a material of the discharge surface treatment electrode 21, whereby a film having strong adhesion can be formed.

Embodiment 2.

FIGs. 5A and 5B are drawings to show the concept of a manufacturing method of a discharge surface treatment electrode according to embodiment 2 of the invention. In the figure, numeral 10 denotes a discharge surface treatment electrode, numeral 11 denotes WC powder, numeral 12 denotes W powder, numeral 23 denotes wax such as paraffin, numeral 24 denotes a vacuum furnace, numeral 25 denotes a high-frequency coil, and numeral 26 denotes a vacuum atmosphere. The wax 23 is mixed with mixed powder of the WC powder 11 and the W powder 12 and they are compressed and molded to form a compacted powder electrode, whereby the mold property can be improved remarkably. However, since the wax 23 is an insulating substance, if it

is left in the electrode in a large amount, the electric resistance of the electrode grows and thus the discharge property is worsened. Then, it becomes necessary to remove the wax 23. FIG. 5A shows how the compact powder electrode into which the wax 23 is mixed is entered in the vacuum furnace 21 and is heated. It is heated in the vacuum atmosphere 26, but may be heated in gas such as hydrogen or argon gas. The compacted powder electrode in the vacuum furnace 24 is high-frequency-heated by the high-frequency coil 25 installed surrounding the vacuum furnace 24. At this time, if the heating temperature is too low, the wax 23 cannot be removed; if the temperature is too high, the wax 23 becomes soot, degrading the purity of the electrode. Thus, it is necessary to keep the temperature at the temperature at which the wax 23 is melted or more and at the temperature at which the wax 23 decomposes to form soot or less. FIG. 6 shows a vapor pressure curve of wax having a boiling point of 250°C as an example. If the atmospheric pressure of the vacuum furnace 24 is kept at the vapor pressure of the wax 23 or less, the wax 23 is evaporated and removed and the discharge surface treatment electrode 10 consisting of WC and W can be provided, as shown in FIG. 5B.

In the description given above, the discharge surface treatment electrode 10 consisting of WC and W and the discharge surface treatment electrode 21 consisting of WC and Fe have been explained, but any other material can be mixed into the

discharge surface treatment electrode depending on the workpiece, of course. For example, if the workpiece is titanium metal, to form a hard film on the workpiece, a film having good compatibility with the base material of the workpiece can be formed by using TiC (titanium carbide) and Ti (titanium), TiC and TiO<sub>2</sub> (titanium oxide), TiC and TiH<sub>2</sub> (titanium hydride), or the like in combination.

#### Industrial Applicability

As described above, the discharge surface treatment electrode and the manufacturing method thereof and the discharge surface treatment method according to the invention are suited for use as industries involving surface treatment for forming a hard film on the surface of a workpiece.

Claims:

1. A discharge surface treatment electrode used for discharge surface treatment of causing discharge to occur between said electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on a surface of the workpiece by discharge energy, characterized in that

the above metal carbide and metal contained in the metal carbide or a compound of that metal or any other metal forming a hard carbide or a compound of that metal are contained as material of said discharge surface treatment electrode.

2. The discharge surface treatment electrode as claimed in claim 1 wherein the metal carbide is metal carbide of metal or a metal compound contained in material of the workpiece.

3. The discharge surface treatment electrode as claimed in claim 2 wherein the material of said discharge surface treatment electrode contains WC and W.

4. A manufacturing method of a discharge surface treatment electrode used for discharge surface treatment causing discharge to occur between said electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on the surface of the workpiece by discharge energy, characterized in that

powder of the metal carbide and powder of the metal contained in the metal carbide or powder of a compound of the



metal or powder of any other metal forming a hard carbide or powder of a compound of that metal are mixed and are compressed and molded to form the discharge surface treatment electrode.

5. The manufacturing method of a discharge surface treatment electrode as claimed in claim 4 wherein wax is added to the material of the discharge surface treatment electrode and then they are compressed and molded and are heated at a temperature at which the wax is melted or more and at a temperature at which the wax is decomposed to produce soot or less, for evaporating and removing the wax to form the discharge surface treatment electrode.

6. A discharge surface treatment method for causing discharge to occur between a discharge surface treatment electrode and a workpiece in work liquid containing carbon and forming a hard film containing metal carbide as a component on a surface of the workpiece by discharge energy, characterized in that

the discharge surface treatment electrode containing the metal carbide and metal contained in the metal carbide or a compound of the metal or any other metal forming hard carbide or a compound of the metal is used.

7. The discharge surface treatment method as claimed in claim 6 wherein the metal carbide is metal carbide of metal or a metal compound contained in material of the workpiece.

## Abstract

WC powder (11) and W powder (12) are mixed and entered in a press mold and compressed and molded, thereby forming a discharge surface treatment electrode (10). Discharge is caused to occur between the discharge surface treatment electrode (10) and a workpiece (16) by a discharge surface treatment power unit (17), whereby a component of the discharge surface treatment electrode (10) melted by discharge heat is deposited on the workpiece (16). W, a component of the discharge surface treatment electrode (10), reacts with C, a component of work liquid (4), to produce WC and together with the WC which is a component of the discharge surface treatment electrode (10) a hard film (20) made of WC is formed on the workpiece (16). The hardness and strength of the hard film formed on the workpiece (16) by the discharge surface treatment can be enhanced.

FIG. 1

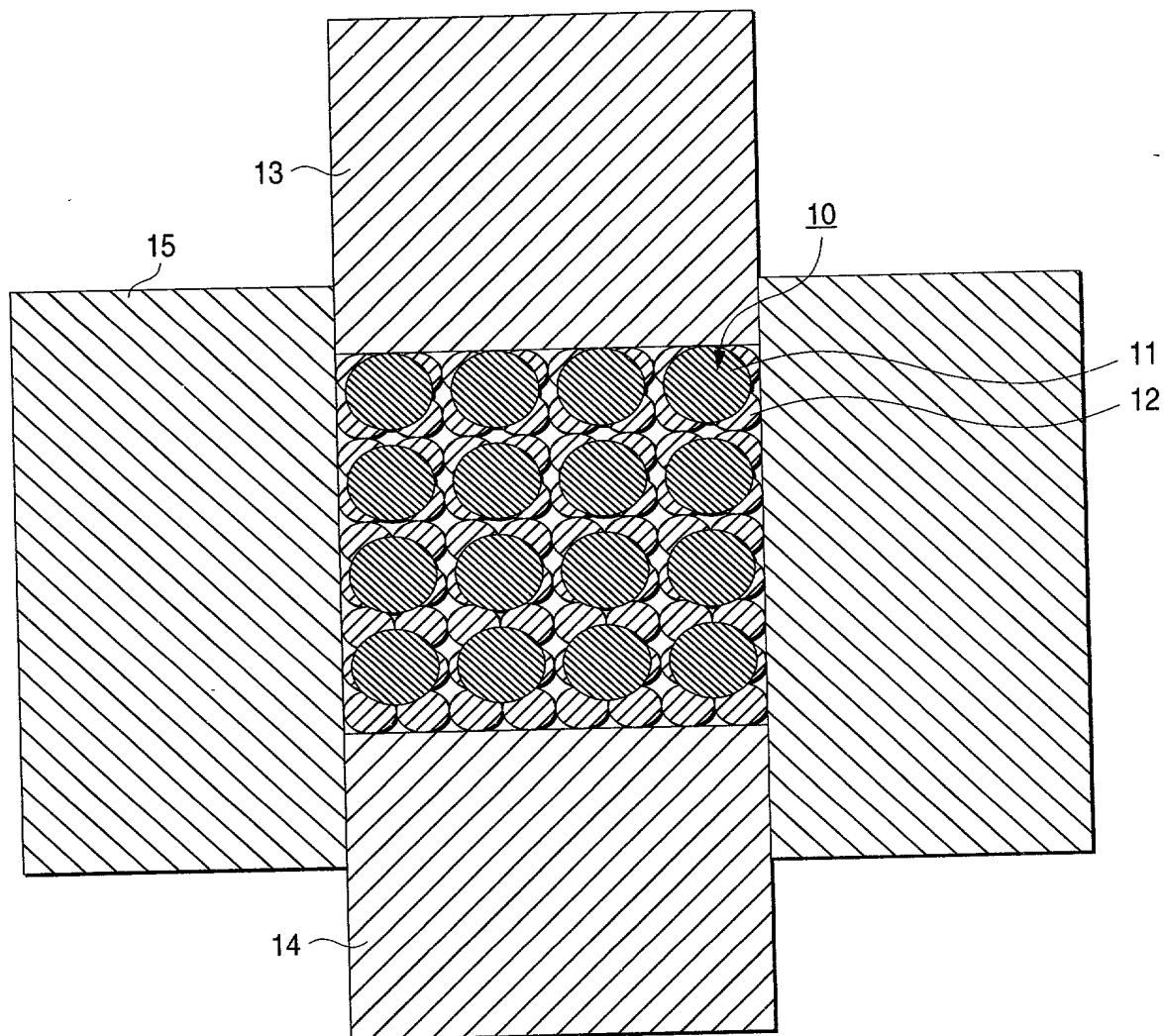
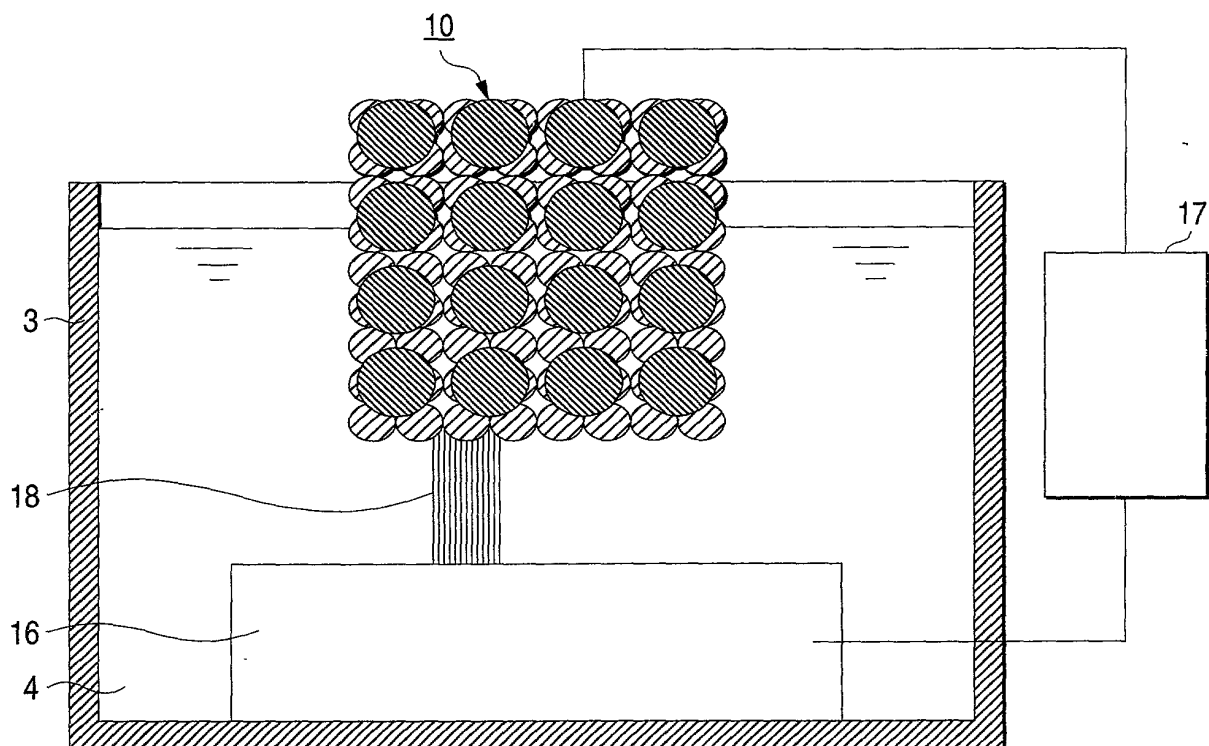


FIG. 2



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FIG. 3A

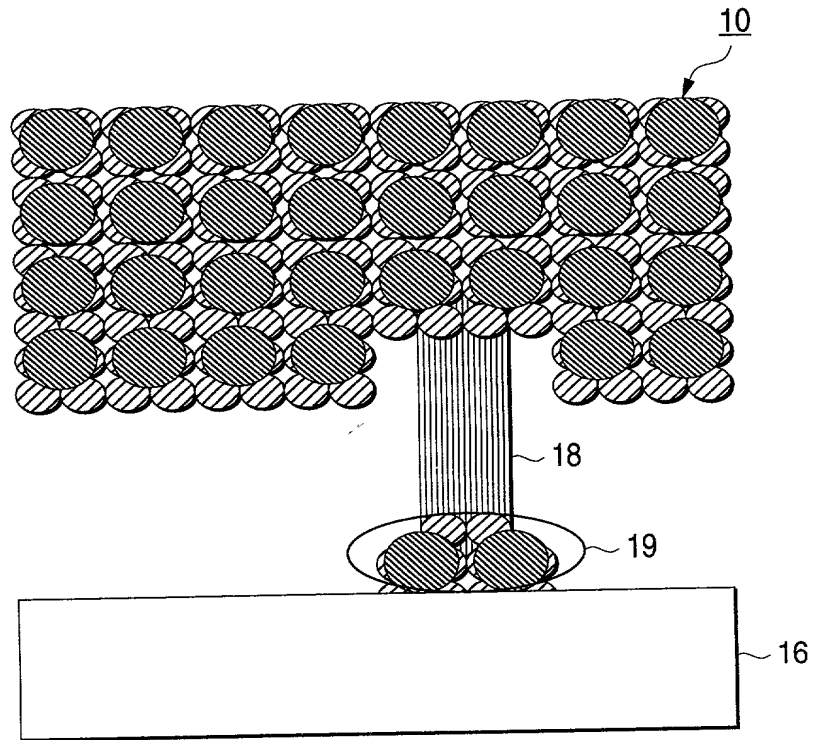


FIG. 3B

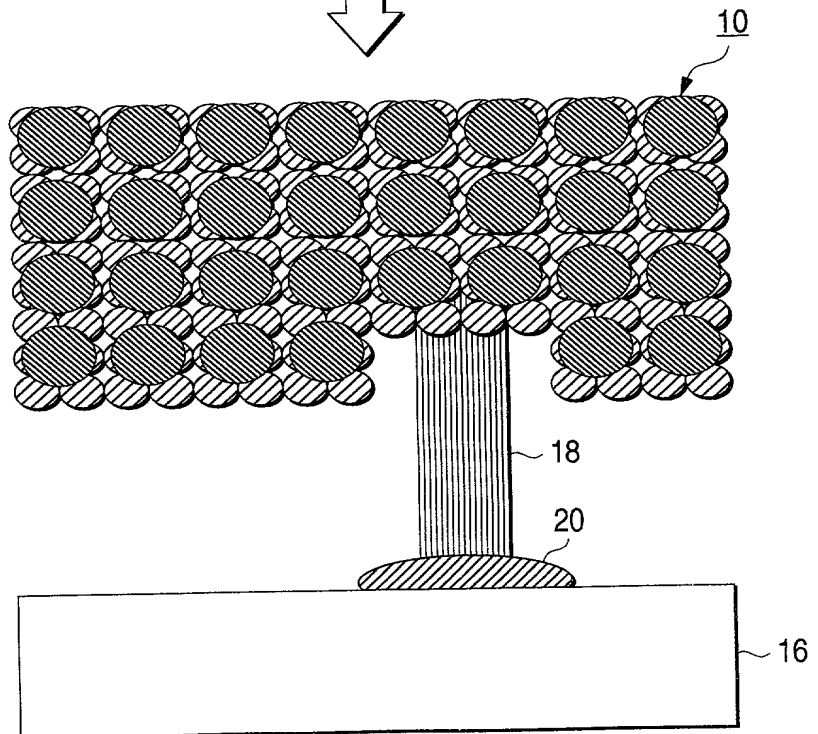
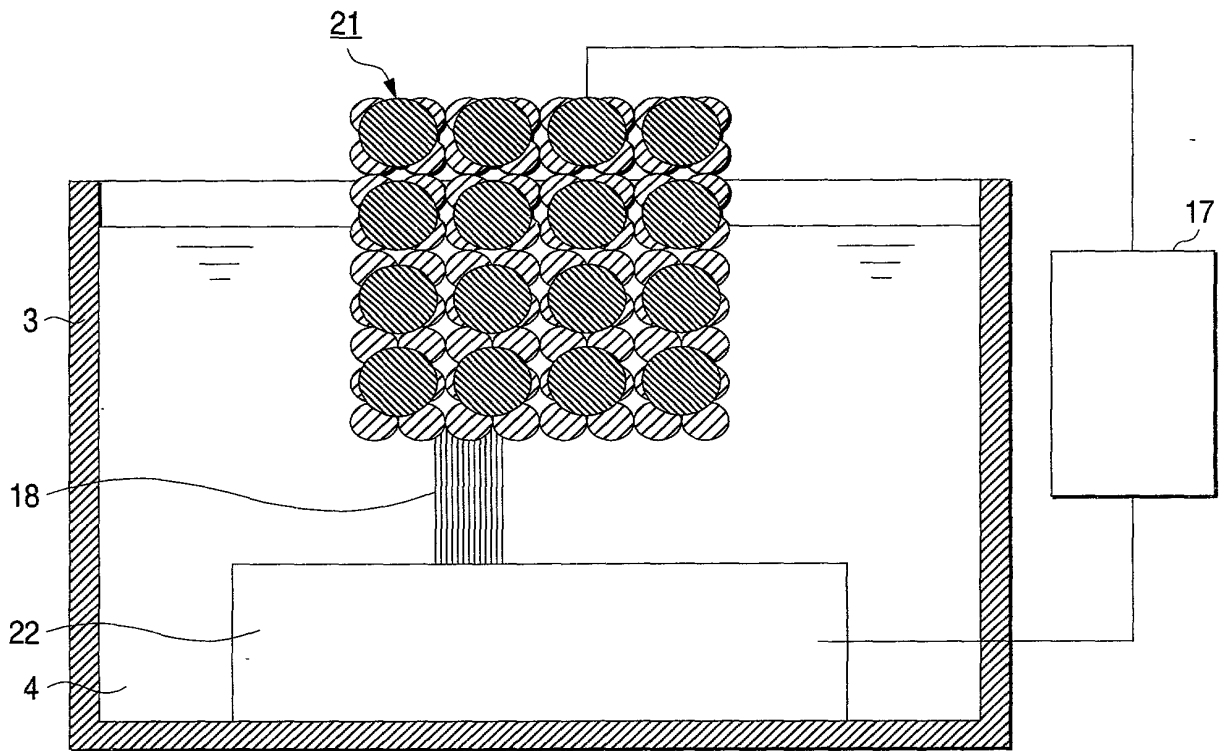


FIG. 4



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FIG. 5A

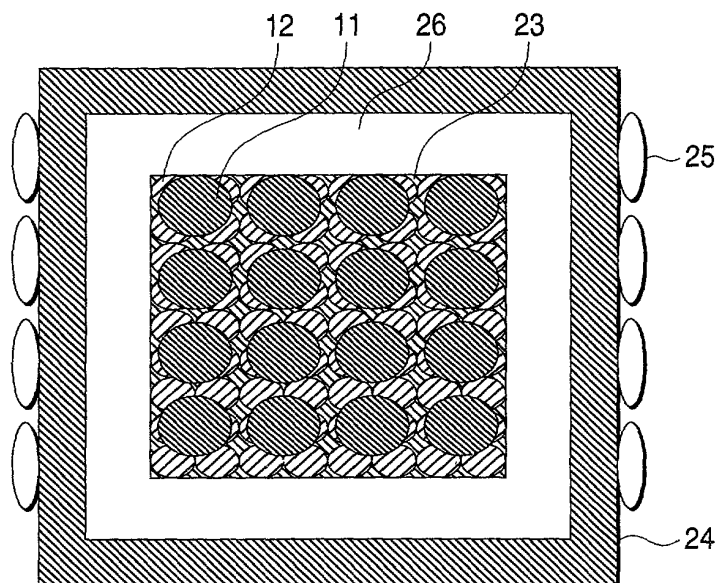
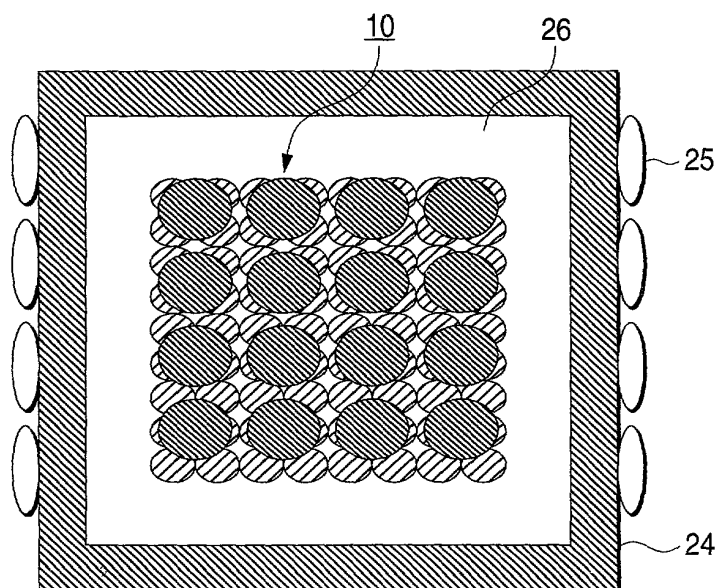


FIG. 5B



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FIG. 6

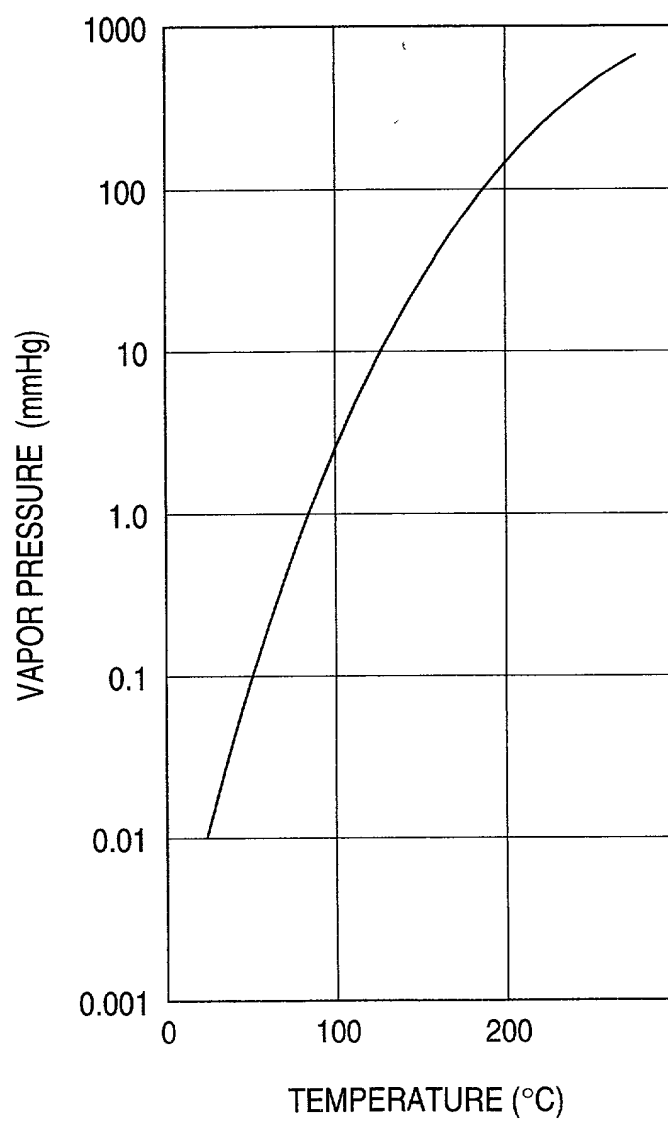
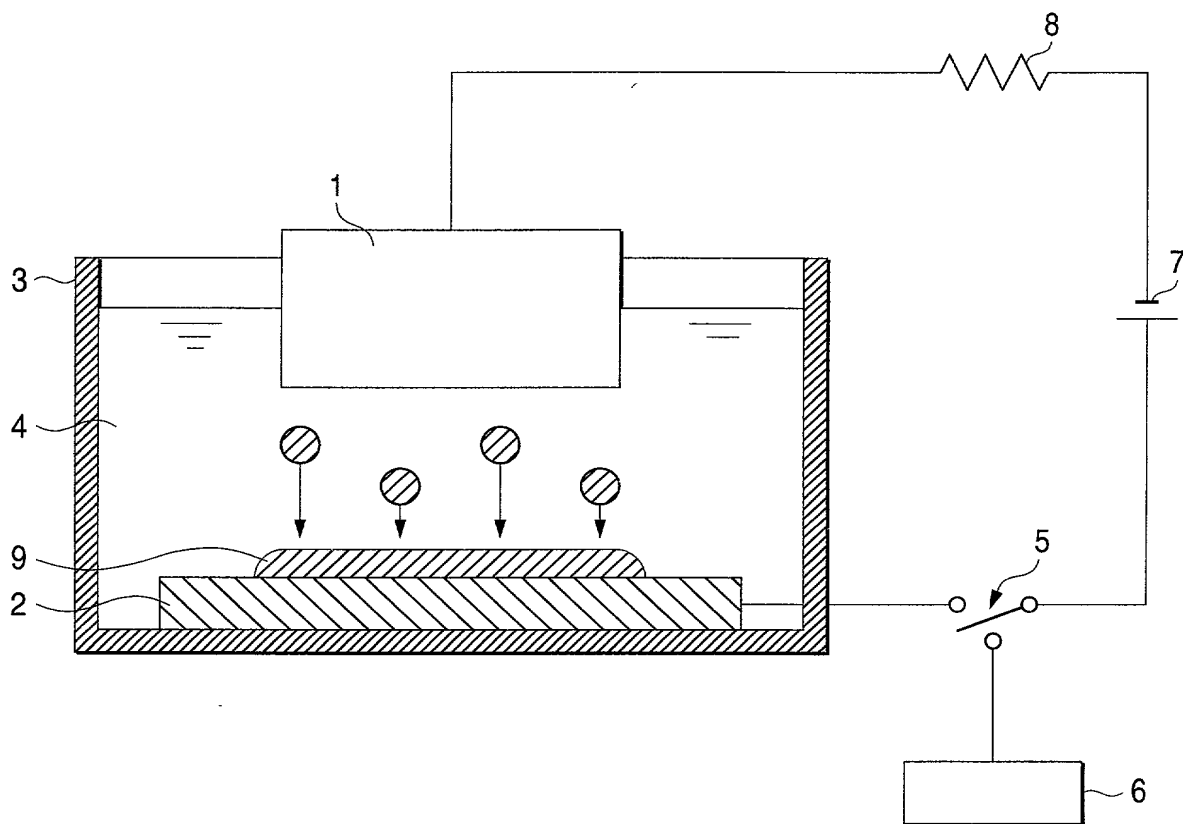




FIG. 7



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# Declaration and Power of Attorney for Patent Application

特許出願宣言書及び委任状

## Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name,

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者(下記の氏名が一つの場合)もしくは最初かつ共同発明者であると(下記の名称が複数の場合)信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

DISCHARGE SURFACE TREATMENT ELECTRODE,

MANUFACTURING METHOD THEREOF AND

DISCHARGE SURFACE TREATING METHOD

上記発明の明細書(下記の欄でX印がついていない場合は、本書に添付)は、

the specification of which is attached hereto unless the following box is checked:

～ 月 日に提出され、米国出願番号または特許協定条約

～ was filed on September 30, 1999  
as United States Application Number or  
PCT International Application Number

国際出願番号を \_\_\_\_\_ とし、

PCT/JP99/05363 and was amended on

(該当する場合) \_\_\_\_\_ に訂正されました。

\_\_\_\_\_ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

# Japanese Language Declaration

(日本語宣言書)

私は、米国法典第35編第119条(a)-(d)項又は第365条(b)項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約第365条(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

## Prior Foreign Applications

外国での先行出願

Priority Not Claimed

優先権主張なし

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)

☐
☐
☐

私は、第35編米国法典119条(e)項に基づいて下記の米国特許出願規定に記載された権利をここに主張致します。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)	(Application No.) (出願番号)	(Filing Date) (出願日)

私は、下記の米国法典第35編第120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約第365条(c)に基づく権利をここに主張します。又、本出願の各請求範囲の内容が米国法典第35編第112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内又は特許協力条約国際出願提出日までの期間中に入手された、連邦規則法典第37編第1条第56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit of Title 35, United States Code Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose any material information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況: 特許許可済、係属中、放棄済)

私は、私自身の知識に基づいて本宣言中で私が行う表明が真実であり、かつ私の入手した情報と私の信ずるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

# Japanese Language Declaration

(日本語宣言書)

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